



Department of Pesticide Regulation



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MEMORANDUM

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DATE: April 1, 2003

SUBJECT: PRELIMINARY MONITORING RESULTS OF SECOND SPINOSAD AERIAL
APPLICATION FOR MEXICAN FRUIT FLY ERADICATION IN VALLEY
CENTER, SAN DIEGO COUNTY (STUDY 216)

The Department of Pesticide Regulation (DPR) conducted monitoring for the second in a series of spinosad aerial applications to eradicate the Mexican fruit fly in San Diego County, California. On January 21 and 22, 2003, the California Department of Food and Agriculture's (CDFA's) contract applicator applied 5,560 gallon (gal) spinosad mixture over 14,754 acres. During this application, DPR staff collected deposition, surface water, air, and fruit samples in the treatment area. A sample was also taken of the spinosad tank mixture. Deposition samples were taken at 26 sites, including three sampling sites within the Keys Creek buffer zone. Surface water samples were taken from Keys Creek. Air samples were collected at four sites and fruit samples were collected from two orchards. The average amount at the 23 deposition sites was $1.64 \mu\text{g}/\text{ft}^2$ (0.072 grams per acre, [g/ac]), 50% of the $3.26 \mu\text{g}/\text{ft}^2$ (0.14 g/ac, or $35.1 \mu\text{g}/\text{m}^2$) target application rate. This was approximately the same as the first application. All three buffer zone deposition samples contained detectable residues, with concentrations ranging from 0.239 to $0.371 \mu\text{g}/\text{ft}^2$. None of the surface water and air samples contained detectable residue. None of the four background fruit samples contained detectable residue. Three of four fruit samples collected after application contained 0.0025 - 0.0039 ppb (ng/g) of spinosad. The tank mix concentration was 0.0078% versus a target concentration of 0.0080%. No organophosphates, carbamates, and chlorinated hydrocarbons were detected in the tank mix sample.

Introduction

CDFA is conducting aerial applications with spinosad to eradicate the Mexican fruit fly infestation in the Valley Center area of San Diego County. The application area consists of 28 mi^2 , of which 23 mi^2 will be treated using aerial applications and five mi^2 around selected water bodies will be treated using ground applications. CDFA plans to aerially apply spinosad every two weeks for two life cycles of the pest to effectuate eradication. For the second application, 5560 gal of spinosad mix were applied over 14,754 acres on January 21 and 22, 2003.



Materials and Methods

The pesticide product and application method used in this application were the same as the first application, using GF-120 NF Naturalyte Fruit Fly Bait (U.S. Environmental Protection Agency Registration Number 62719-498), containing 0.020% spinosad by weight (mixture of spinosyn A and spinosyn D) as the active ingredient. For application, the GF-120 NF was diluted with water to a tank mix target concentration of 0.0080% by weight of spinosad or 0.363 grams per gal. The spinosad (active ingredient) target application rate was $3.26 \mu\text{g}/\text{ft}^2$ (0.142 g/acre, or $35.1 \mu\text{g}/\text{m}^2$). In this application, 5560 gal of spinosad mix was applied over 14,754 acres (23.05 mi^2). The application started on January 21 at 8:00 p.m. and ended on January 22 at 4:41 a.m. The application was made using three fixed-wing aircraft, each with a swath width of 100 feet (ft), sprayed in east and west directions at an altitude of approximately 500 ft. CDFA established buffer zones around several water bodies and excluded them from the aerial application.

Spinosad residues were measured in deposition, surface water, air, fruit, and spray tank mixture samples. Deposition samples were collected using one ft^2 mass deposition sheets. Deposition sheets were set at 23 sampling sites dispersed throughout the treatment area (Figure 1). In addition, three deposition sites were sampled within the buffer zone around Keys Creek. The sheets were set at sampling sites before application and collected after application.

Background water samples were collected before application from Keys Creek (Figure 1) on January 21. Water samples were also collected after application on January 22.

Air samples were collected from four sites (Figure 1) for background, application, and post-application using XAD-2/glass-fiber filter tubes (SKC#226-30-16) and personal air sampling pumps (SKC#224-PCXR8) at a constant flow rate of 3000 ml/min. At each of the four sites, a single sampler was set approximately four to six feet above the ground and protected from direct application. Background air samples were taken for approximately 24 hrs before application; application samples were collected for the duration of application; and post-application samples were taken for 24 hrs after application.

Fruit samples were collected from two orchards (Figure 1). At each sampling site, two grapefruit trees were picked randomly, and would be sampled for the duration of the monitoring study. From each sampling tree, two samples were collected, one from the upper and the other from the lower portions of the tree at randomly chosen compass direction. For each sample, two grapefruit were taken from different sides of the tree, placed into a stainless steel bucket, and covered with stainless steel lid. Background fruit samples were collected 4 - 5 hrs before application and application fruit samples were collected 4 - 5 hrs after application.

Deposition, air, and fruit samples were stored on dry ice; water and tank mix samples were stored on ice until delivery to the CDFA Center for Analytical Chemistry for analysis. All samples were analyzed for spinosyn A and D, as well as spinosyn B, a breakdown product. The deposition samples were extracted with methanol and analyzed using liquid chromatograph with a tandem mass spectrometer detector (LC/MS/MS) providing a quantitation limit of $0.1 \mu\text{g}/\text{ft}^2$. The water samples were extracted with methylene chloride and analyzed using a LC/MS/MS, providing a quantitation limit of 0.05 ppb. Air samples were extracted with methanol and methylene chloride, and analyzed using LC/MS/MS providing a quantitation limit of $0.5 \mu\text{g}/\text{sample}$ ($0.116 \mu\text{g}/\text{m}^3$). Grapefruit samples were extracted with acetonitrile and water, and analyzed using LC/MS/MS providing a quantitation limit of 1 ppb. Containers for the fruit samples were rinsed with methanol and analyzed separately using LC/MS/MS providing a quantitation limit of approximately 0.0024 ppb (ng/g) fruit basis. The tank mix sample was extracted with acetone and analyzed using a high-performance liquid chromatograph and ultraviolet detector, providing a quantitation limit of one ppm (0.0001%). The tank mixture sample was also screened for organophosphates, carbamates, and chlorinated hydrocarbons.

Results

Results of the deposition samples are listed in Table 1. All 23 deposition samples had a detectable amount of spinosad, ranging from 0.25 to $5.55 \mu\text{g}/\text{ft}^2$ and averaged $1.64 \mu\text{g}/\text{ft}^2$ (total spinosyns A, D, and B), 50% of the $3.26 \mu\text{g}/\text{ft}^2$ target application rate. These results were very similar to the first application (Figure 2).

All three samples from buffer zone sites had detectable amounts of spinosad, ranging from 0.24 to 0.37 and averaged $0.30 \mu\text{g}/\text{ft}^2$ (Table 2). For the first application, one of the three buffer zone sites had a detectable amount of spinosad.

Spinosad was not detected in any of the surface water samples (Table 3), as in the first application.

Air samples (Table 4) had no detectable spinosad. No air samples were collected during the first application.

None of the four background fruit samples contained detectable amount of spinosad. Although none of the grapefruit collected after application had detectable spinosad, the rinse from three of the four sample containers did contain measurable amounts of spinosad. Dividing the amount of spinosad detected by the fruit sample weight, gives concentrations ranging from 0.0025 to 0.0039 ppb (Table 5) for the application fruit samples. This concentration is less than the quantitation limit in the grapefruit of 1 ppb. The positive finding in the sample container rinse strongly suggests that spinosad was present on the fruit surface, but not detected due to the higher quantitation limit of the fruit itself. The grapefruit samples collected for this application were not

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mature, and therefore are unsuitable for determining legal compliance with the tolerance. All application samples were less than the 300 ppb tolerance level. No fruit samples were collected during the first application.

Concentration for the tank mixture sample was 0.0078%, versus the target concentration of 0.0080%. No organophosphate, carbamate, or chlorinated hydrocarbon pesticides analyzed were detected in the tank mix sample. A total volume of 5560 gal of the tank mixture was applied to 14,754 acres (23.05 mi²). If the tank mix contained the target concentration (0.0080%), the actual application rate would be 3.14 µg/ft² or 96% of the target rate (3.26 µg/ft², 0.14 g/ac, or 35.1 µg/m²), compared to 91% in the first application.

During the application, it was a clear and calm night with temperature ranging from 39 – 47 °F and wind speed 0 - 3 miles per hour.

Results reported here are also available at DPR's website <<http://www.cdpr.ca.gov/docs/mexfly/>>. For the fruit samples, the surface of the fruit and whole fruit will be analyzed separately in the later applications.

Table 1. Monitoring results for deposition samples. The amount of total spinosad is sum of the individual spinosyns (A, D, and B). The target amount is 3.26 $\mu\text{g}/\text{ft}^2$.

Site Code	Spinosad ($\mu\text{g}/\text{ft}^2$)			Total ^a
	A	D	B	
1	0.258	Tr ^b	Tr	0.382
2	2.830	0.443	0.406	3.679
3	0.595	Tr	Tr	0.719
4	0.178	Tr	Tr	0.302
5	0.981	0.132	0.206	1.319
6	1.550	0.256	0.269	2.075
7	4.340	0.654	0.551	5.545
8	2.910	0.400	0.524	3.834
9	1.610	0.272	0.103	1.985
10	0.372	Tr	0.172	0.604
11	1.350	0.181	0.251	1.782
13	1.680	0.236	0.309	2.225
14	0.780	0.113	0.130	1.023
15	0.704	0.100	0.122	0.926
16	2.480	0.370	0.647	3.497
17	0.476	Tr	0.134	0.670
18	0.684	0.105	0.114	0.903
19	0.877	0.125	0.146	1.148
20	0.168	Tr	Tr	0.292
22	0.188	Tr	ND ^c	0.248
23	0.484	Tr	Tr	0.608
25	1.130	0.154	0.185	1.469
26	2.030	0.293	0.213	2.536
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Average	1.246	0.188	0.209	1.642
Std. Dev.	1.071	0.157	0.173	1.382
Minimum	0.168	0.060	0.000	0.248
Maximum	4.340	0.654	0.647	5.545

^a Sum of detected spinosyns (A, D, and B), wherever trace amount (less than the quantitation limit 0.1 $\mu\text{g}/\text{ft}^2$) was detected in the lab analysis, the quantity of (quantitation limit + detection limit)/2 $\mu\text{g}/\text{ft}^2$ was used to calculate the sum and average spinosyns in this report.

^b Trace amount less than the 0.1 $\mu\text{g}/\text{ft}^2$ quantitation limit detected

^c None Detected, with a detection limit of 0.008, 0.020, and 0.028 $\mu\text{g}/\text{ft}^2$ spinosyn A, D, and B respectively

Table 2. Monitoring results for buffer zone deposition samples. The amount of total spinosad is sum of the individual spinosyns (A, D, and B).

Sampling		Spinosad ($\mu\text{g}/\text{ft}^2$)			Total ^a
Date	Site	A	D	B	
1/22/2003	12	0.311	Tr ^b	ND ^c	0.371
1/22/2003	21	0.175	ND	Tr	0.239
1/22/2003	24	0.215	ND	Tr	0.279
Average					0.296

^a Sum of detected spinosyns (A, D, and B), wherever trace amount (less than the quantitation limit $0.1 \mu\text{g}/\text{ft}^2$) was detected in the lab analysis, the quantity of (quantitation limit + detection limit)/2 $\mu\text{g}/\text{ft}^2$ was used to calculate the sum and average spinosyns in this report.

^b Trace amount less than the $0.1 \mu\text{g}/\text{ft}^2$ quantitation limit detected

^c None Detected, with a detection limit of 0.008, 0.020, and $0.028 \mu\text{g}/\text{ft}^2$ spinosyn A, D, and B respectively

Table 3. Monitoring results for surface water samples. The amount of spinosad is shown as the individual spinosyns (A, D, and B).

Sampling		Sampling Interval	Spinosyn (ppb)			pH
Date	Site		A	D	B	
1/21/2003	28	Background	ND ^a	ND	ND	7.89
1/22/2003	28	Application	ND	ND	ND	7.77

^a None Detected, with a detection limit of 0.025 ppb for each individual spinosyn.

Table 4. Monitoring results for air samples. The amount of spinosad is shown as the individual spinosyns (A, D, and B).

Sampling			Spinosyn ($\mu\text{g}/\text{m}^3$)		
Date	Site	Interval	A	D	B
1/21/2003	3	Background	ND ^a	ND	ND
1/21/2003	7	Background	ND	ND	ND
1/21/2003	20	Background	ND	ND	ND
1/22/2003	3	Application	ND	ND	ND
1/22/2003	7	Application	ND	ND	ND
1/22/2003	19	Application	ND	ND	ND
1/22/2003	20	Application	ND	ND	ND
1/23/2003	3	Post-application	ND	ND	ND
1/23/2003	7	Post-application	ND	ND	ND
1/23/2003	19	Post-application	ND	ND	ND
1/23/2003	20	Post-application	ND	ND	ND

^a None Detected, with a detection limit of 0.0275, 0.0343, and $0.0310 \mu\text{g}/\text{m}^3$ spinosyn A, D, and B, respectively

Table 5. Monitoring results for fruit samples. The amount of total spinosad is sum of the individual spinosyns (A, D, and B).

Sampling			Fruit Spinosyn (ppb)			Container Rinse Spinosyn (ppb)			Total ^a
Site	Interval	Portion	A	D	B	A	D	B	
3	Background	upper	ND ^b	ND	ND	ND	ND	ND	0
3	Background	lower	ND	ND	ND	ND	ND	ND	0
27	Background	upper	ND	ND	ND	ND	ND	ND	0
27	Background	lower	ND	ND	ND	ND	ND	ND	0
3	Application	upper	ND	ND	ND	0.0025	ND	ND	0.0025
3	Application	lower	ND	ND	ND	0.0027	ND	ND	0.0027
27	Application	upper	ND	ND	ND	0.0039	ND	ND	0.0039
27	Application	lower	ND	ND	ND	ND	ND	ND	0

^a Sum of detected spinosyns (A, D, and B) in fruit and container rinse.

^b None Detected, with a detection limit for fruit samples of 0.903, 0.716, and 0.959 ppb spinosyn A, D, and B, respectively, and a quantitation limit for container rinse of 3 ng/sample (~0.0024 ppb). Detection limit for container rinse was not available.

Table 6. Monitoring results for tank sample. The amount of total spinosad is sum of the individual spinosyns (A, D, and B). The target tank mix concentration is 0.008%.

Date	Type	A	D	B	Total
1/21/03	Tank Mix	0.0068	0.001	ND ^a	0.0078

^a None Detected, with a detection limit of 0.0001%

Figure 1. Sampling sites for the second serial spinosad application (January 21-22, 2003)

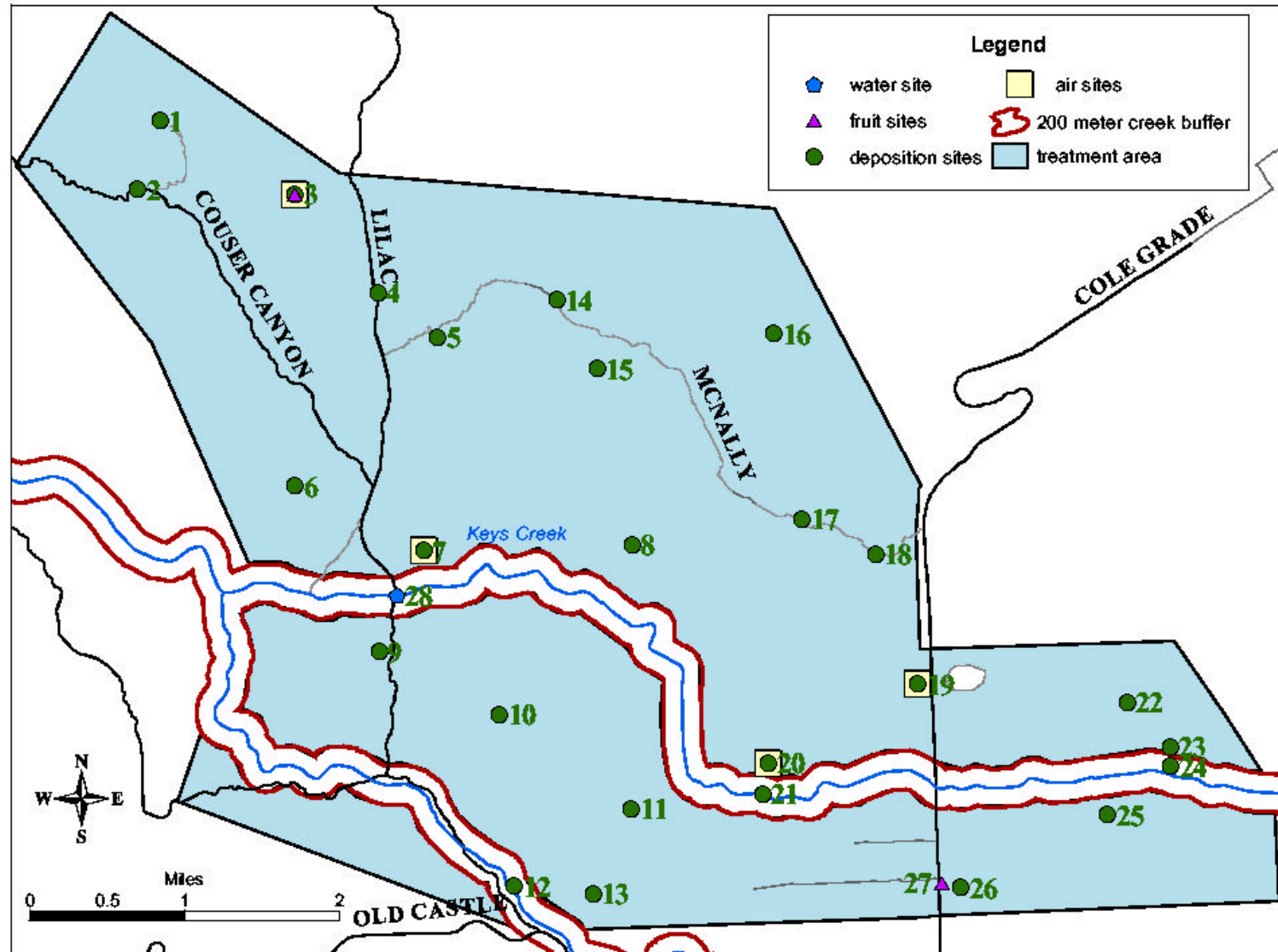


Figure 2. Comparison of average of deposition spinosad in the first (Jan, 7-8 and 9-10) and second (January 21-22) applications. Error bars indicate ± 1 standard error.

